



Next Generation Ambient Air Monitoring for Benzene and Toluene Compared with Traditional Methods at the Fenceline of an Indiana Oil Refinery

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Significance



- EPA's National Air Toxics Assessment (NATA)¹ shows benzene is one of the two top contributors to overall cancer risk in the U.S. from inhalation exposure.
- Toluene is a neurotoxin and an important tracer for mobile sources and industrial emissions.
- Air monitoring for VOCs is relatively expensive, because of required infrastructure and highly-skilled laboratory services.
- Highest benzene concentrations near industrial sites, most notably coke ovens & petroleum refineries.

1. Summary of Results for the 2005 National-Scale Assessment:
http://www.epa.gov/ttn/atw/nata2005/05pdf/sum_results.pdf

Petroleum Refinery Sector Risk & Technology Review; New Source Performance Standards

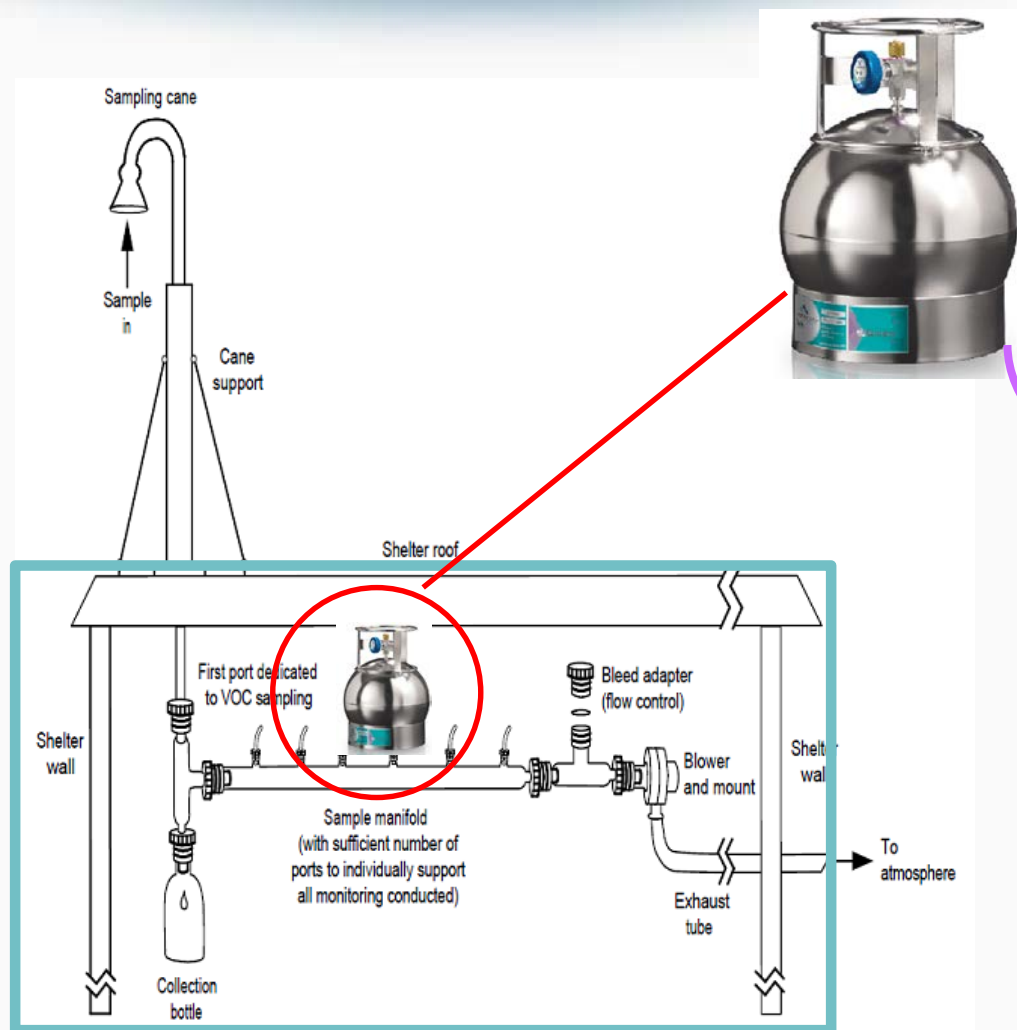


- Additional emissions control requirements
- Application of a new air monitoring method to detect fugitive emissions
- EPA set an annual average benzene concentration standard at the refinery fence line, measured using 2-week integrated samples placed around the refinery fence line perimeter.
- ***Is this new monitoring method any good?!***

EPA's current method – 24-hr canister sample, TO-15 in lab



Used in the National Air Toxics
Trends Station (NATTS) network



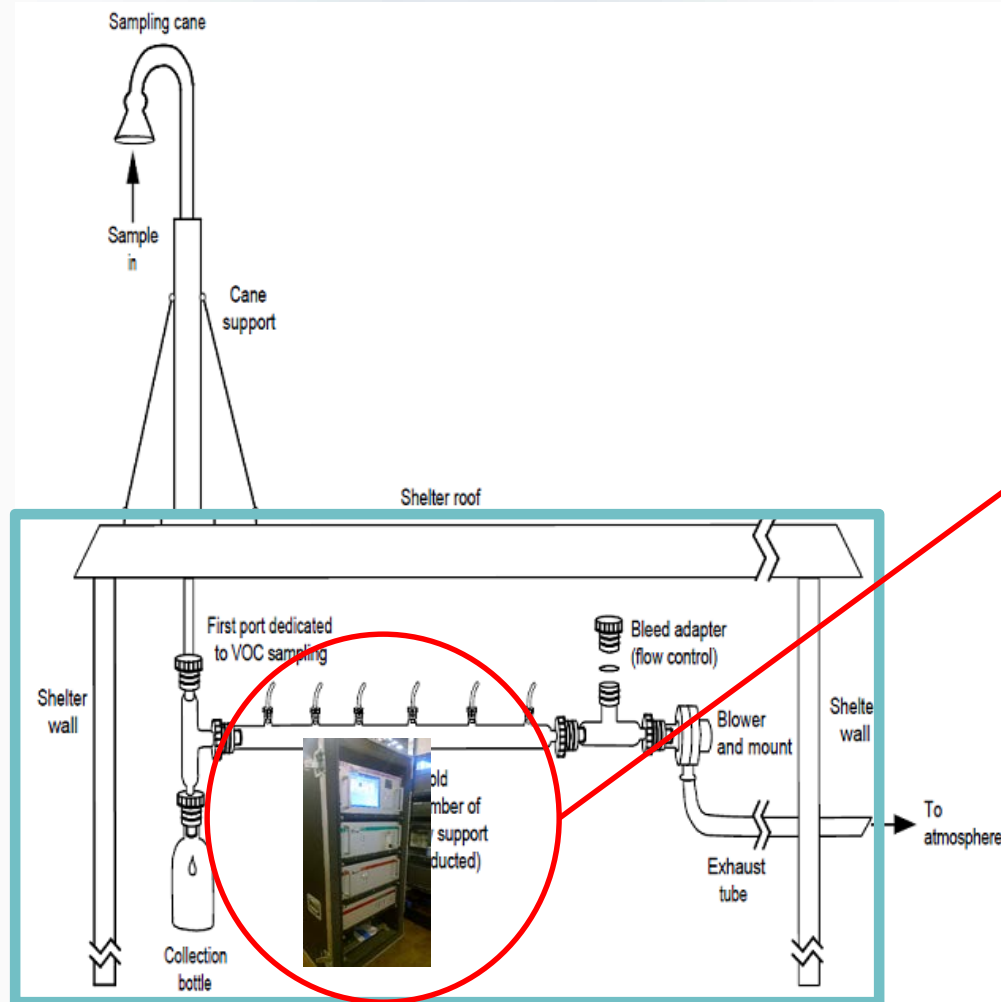
GC-MS



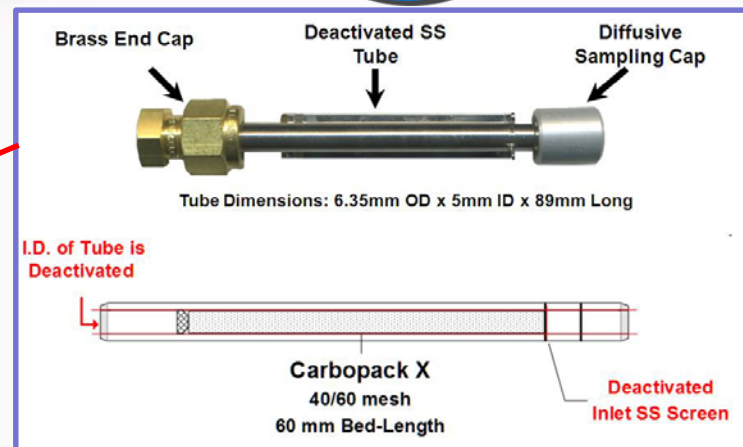
Alternative to current method – Hourly data in field via auto-GC



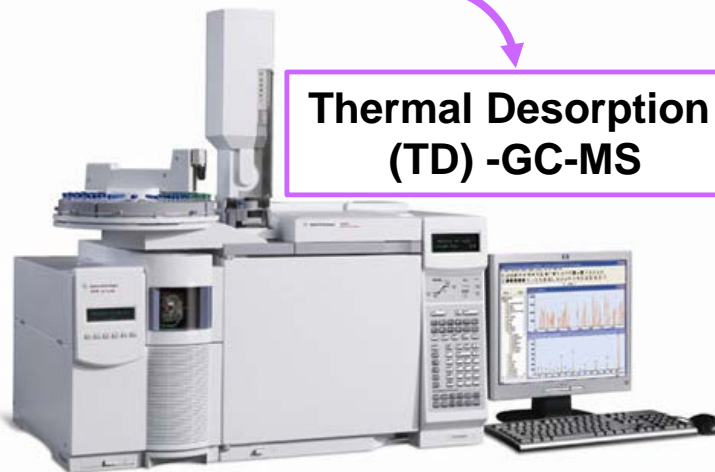
Used at Photochemical Assessment
Monitoring Stations (PAMS) sites



New method – Passive tubes, collection via Method 325A, analysis via Method 325B



**Thermal Desorption
(TD) -GC-MS**



This study



- Follow-up to an initial feasibility study led by EPA's Office of Research and Development (ORD) and Regions 3, 5, 6, & 8: "Collaborative Evaluation of a Low-Cost Volatile Organic Compounds Passive Sampling Method & Analytical Laboratory Intercomparison"
- **Our objective is to quantify the comparability of the new passive tube method to EPA's recommended method for VOC sample collection – canisters.**
- Added benefit: we received permission to piggyback sampling on an existing fenceline network of auto-GC stations at an Indiana refinery.

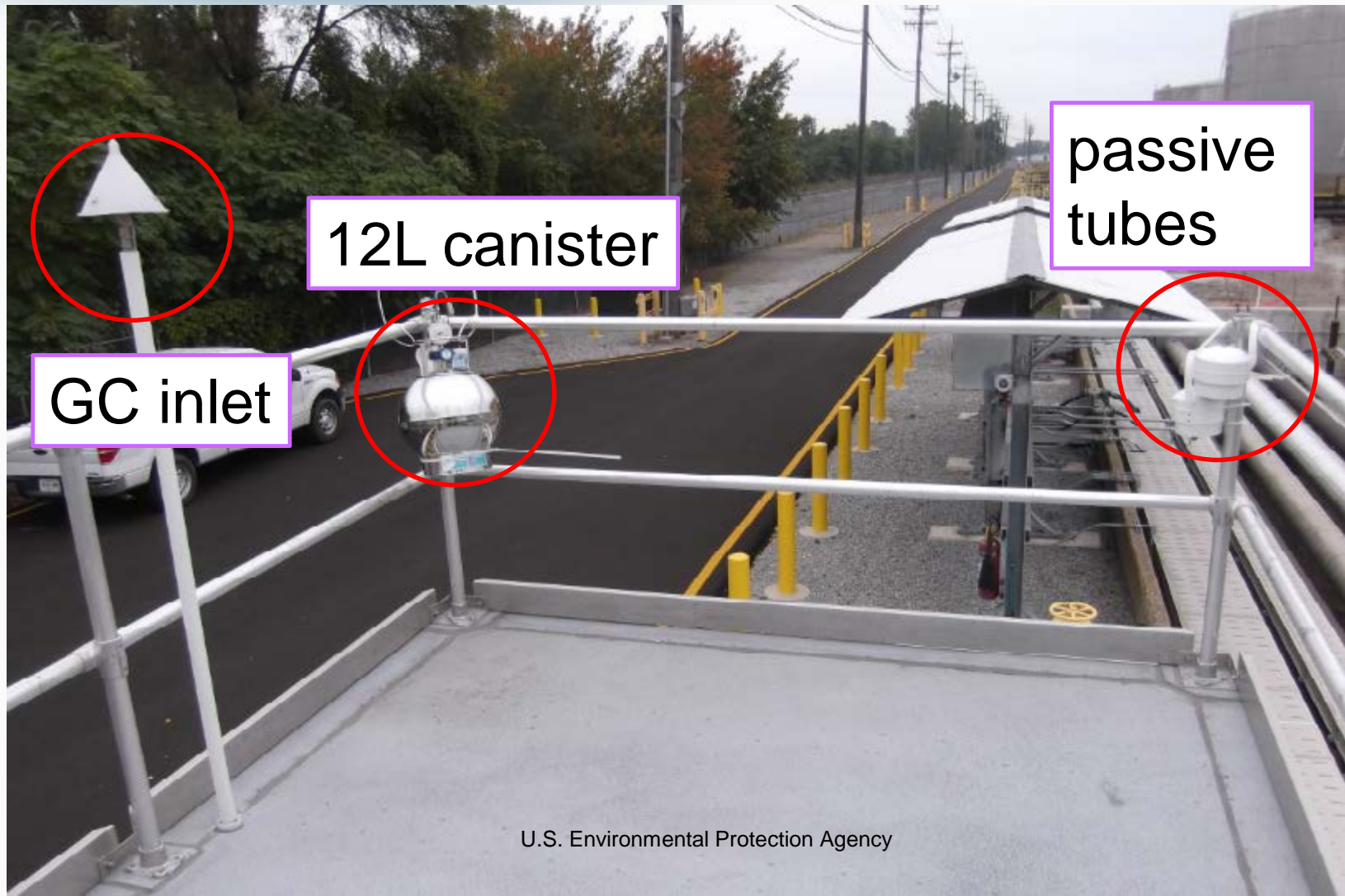
BP Refinery, Whiting, Indiana



- Four-station fenceline network is result of 2012 agreement between refinery, regulators, & private citizen groups.
- BP committed to provide comprehensive air quality information regarding conditions at the fenceline via this public website:

<http://raqis.radian.com/pls/raqis/bpw.whiting>

We collected 8 sets of 1-week samples on top of GC trailers



Challenges - practical



- Scientists not accustomed to extensive safety and security procedures at a refinery
 - field staff underwent safety training
 - fire retardant suit, reflective vest, hardhat, protective gloves, etc.
 - check in/out at each sampling location
 - everything took longer than expected
- First sampling event incomplete due to rain and risk of lightning. Several hours under “stop work” orders for outdoor activities.



Challenges - technical



- EPA-CRL provided canisters under vacuum
 - passive flow regulators on inlet, set to fill in 7 days
 - if canisters fill too quickly, they equilibrate with environment and gases diffuse in/out
- EPA-ORD provided multiple tubes each week
 - blanks & duplicates, shipped overnight in coolers
- BP posts 1-hour data on public website
 - should be 168 measurements per week
 - about 25% missing values; up to 40% nondetects

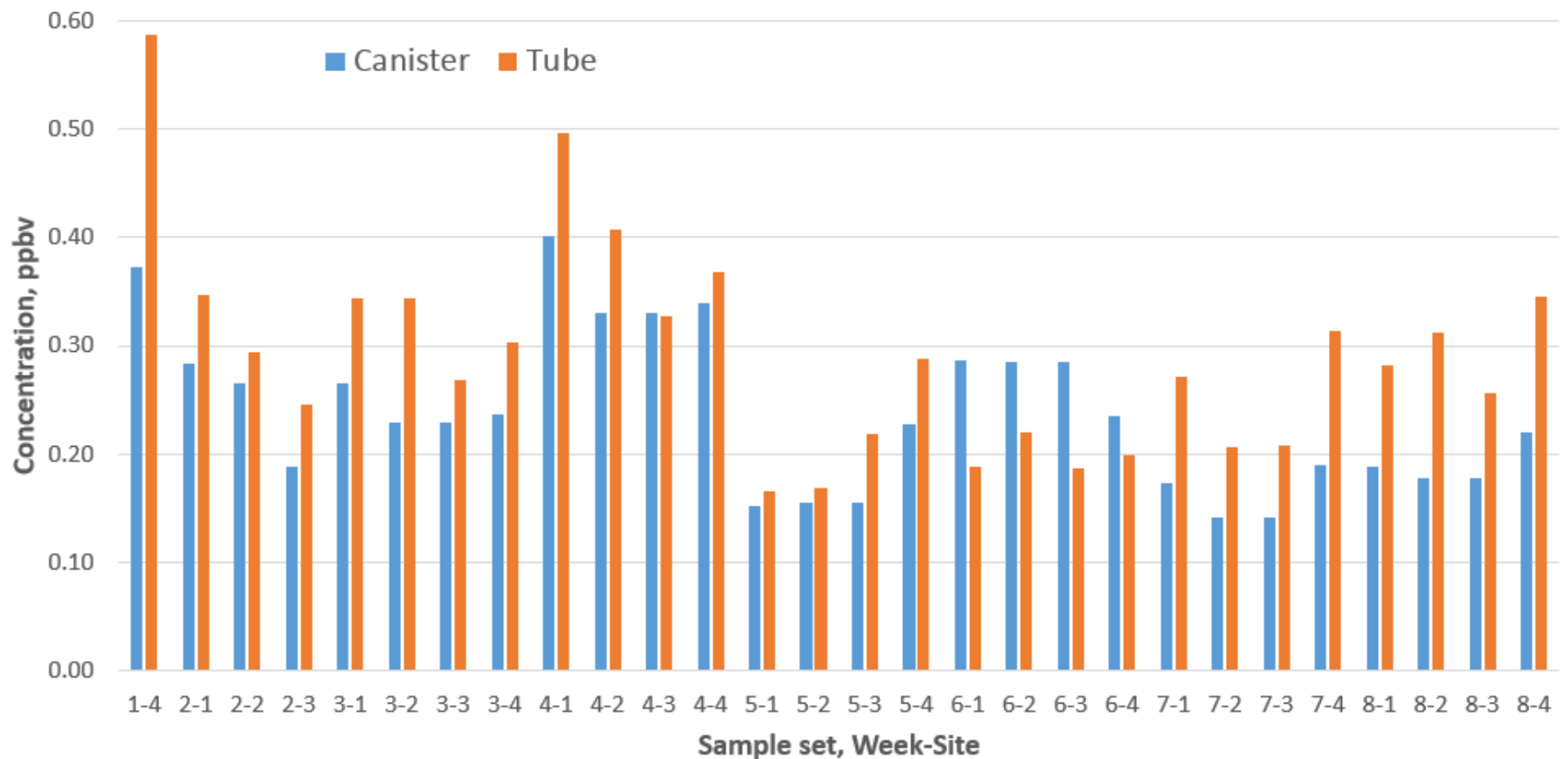
Results



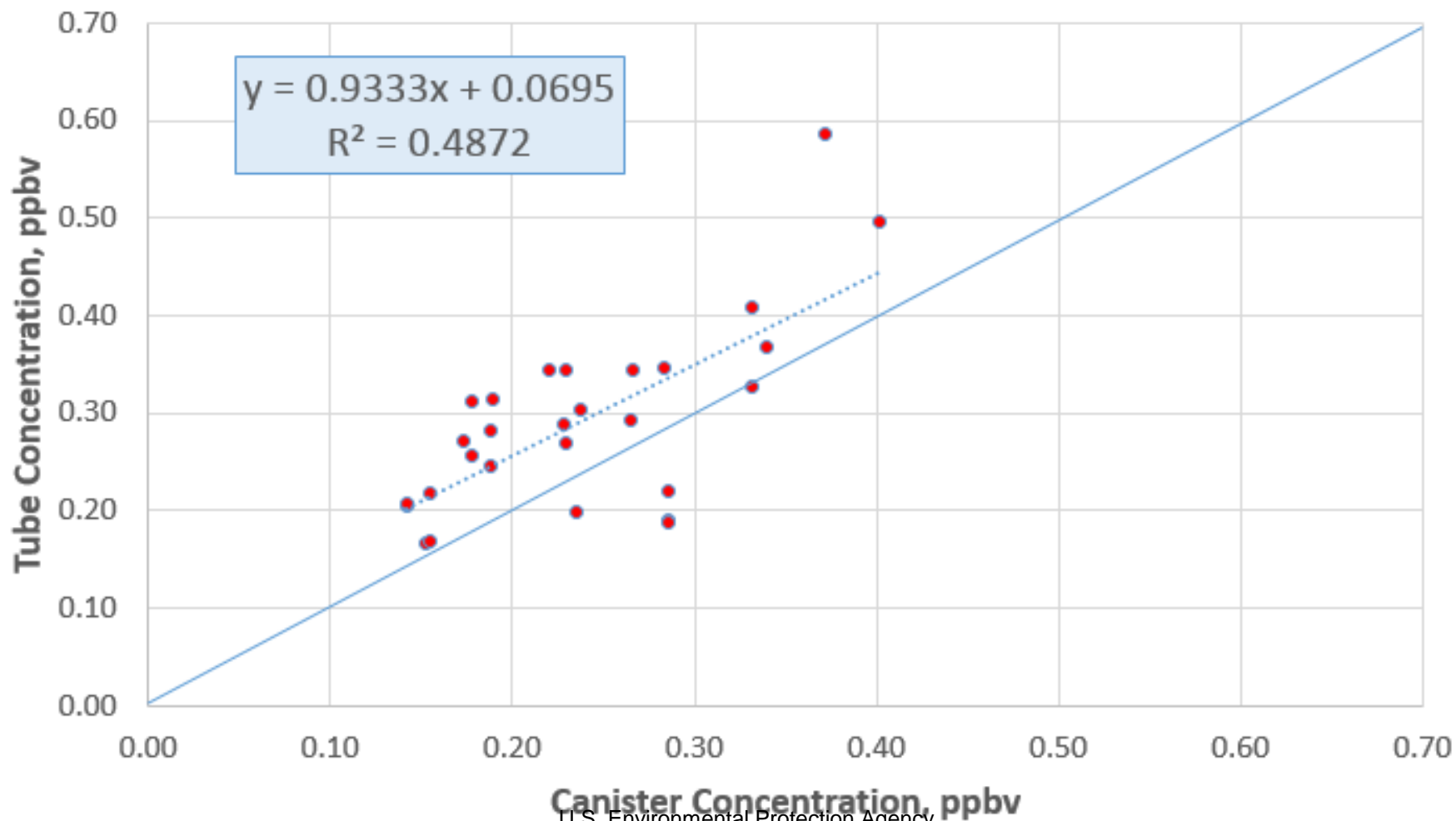
- 28 valid sets (of possible 32) 1-week paired canisters & tubes collected; analyzed at CRL and ORD, respectively
- Comparison methods
 - Plotted linear regression for full dataset
 - Correlation (R-squared), intercept, and slope
 - Calculated Relative Percent Difference (RPD) for each pair

$$\%RPD = \frac{(C_1 - C_2)}{\frac{(C_1 + C_2)}{2}} * 100\%$$

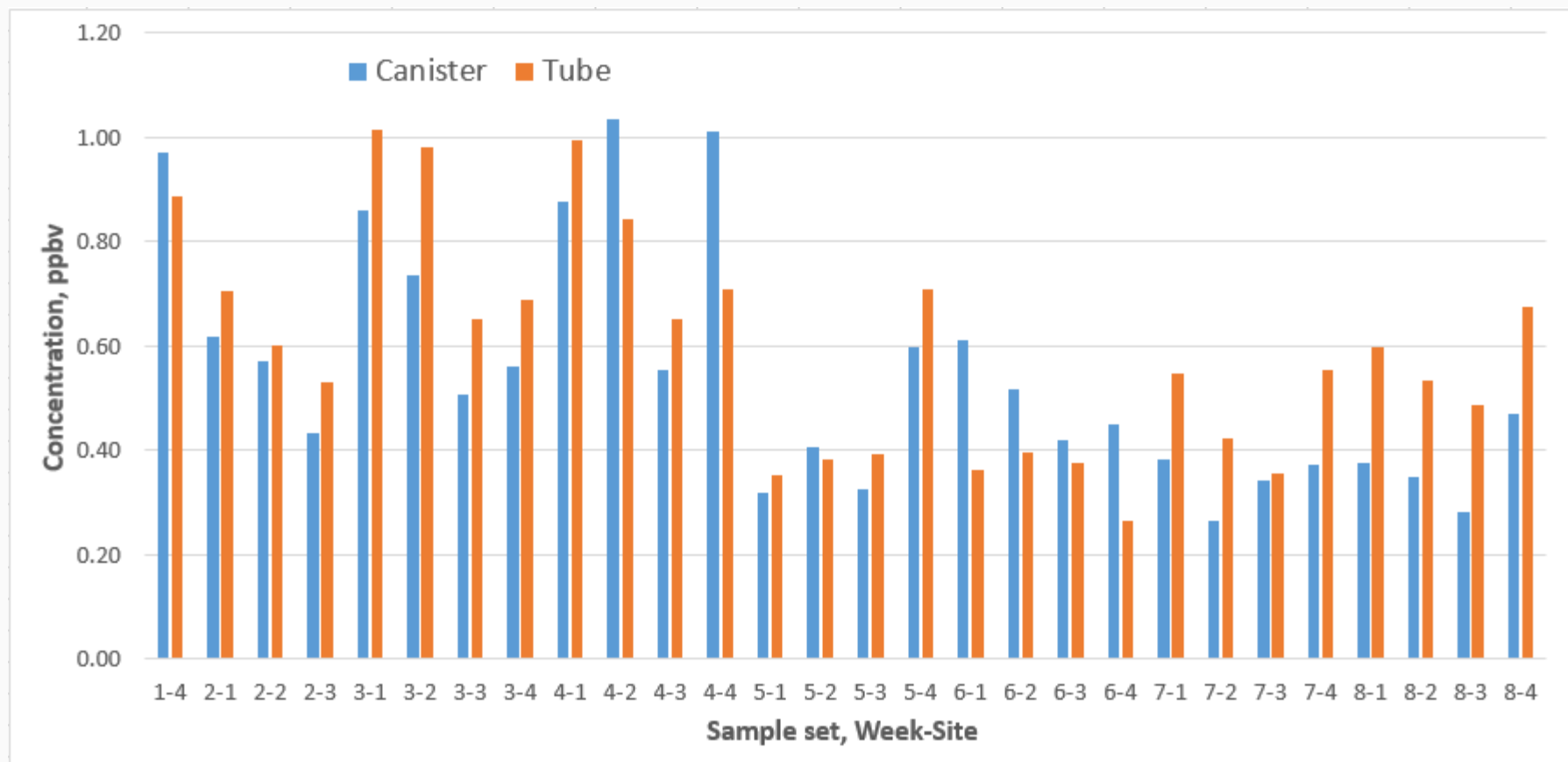
Benzene – Canister and Tube Results



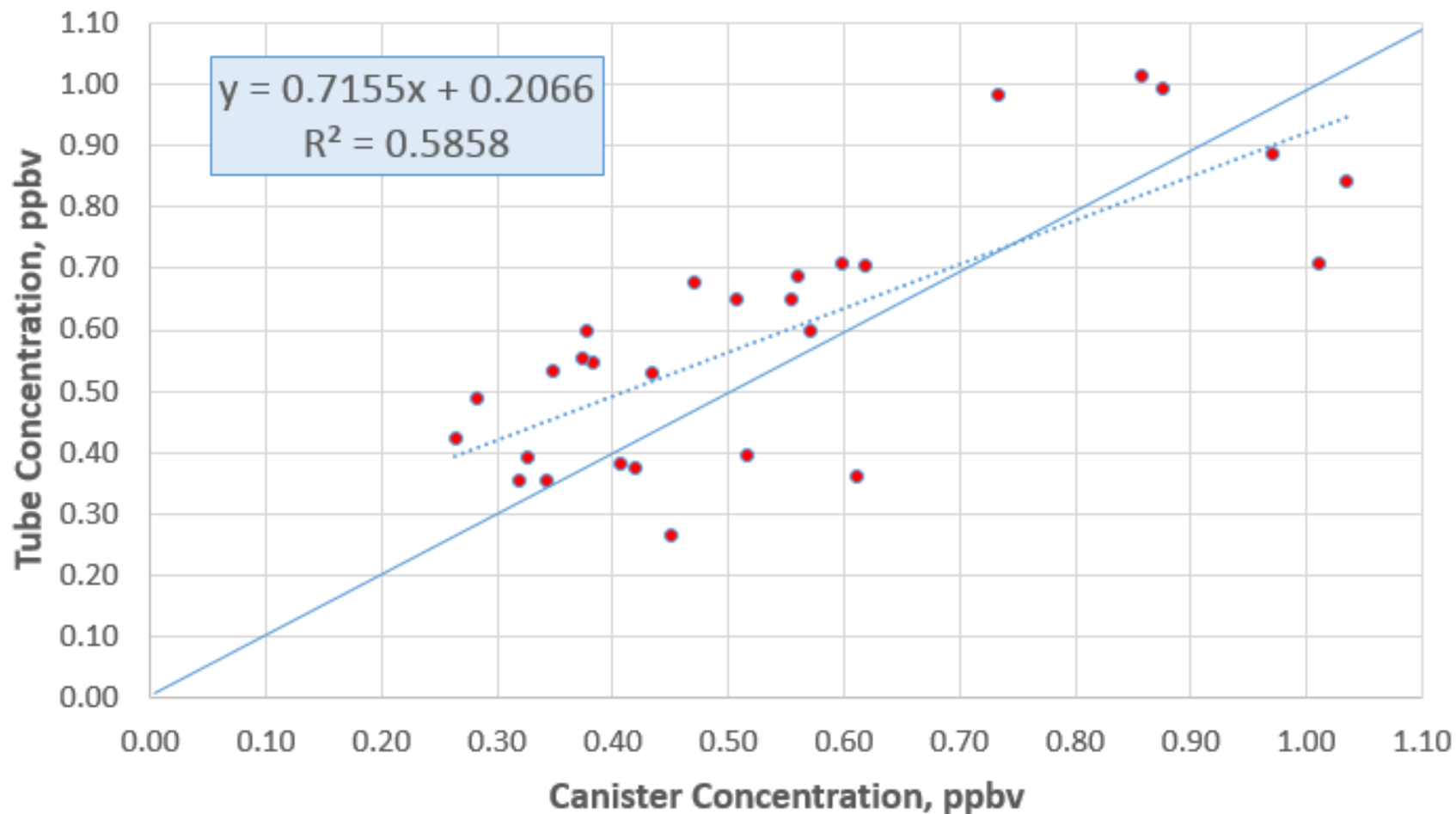
Benzene – Canister vs. Tube Regression



Toluene – Canister and Tube Results

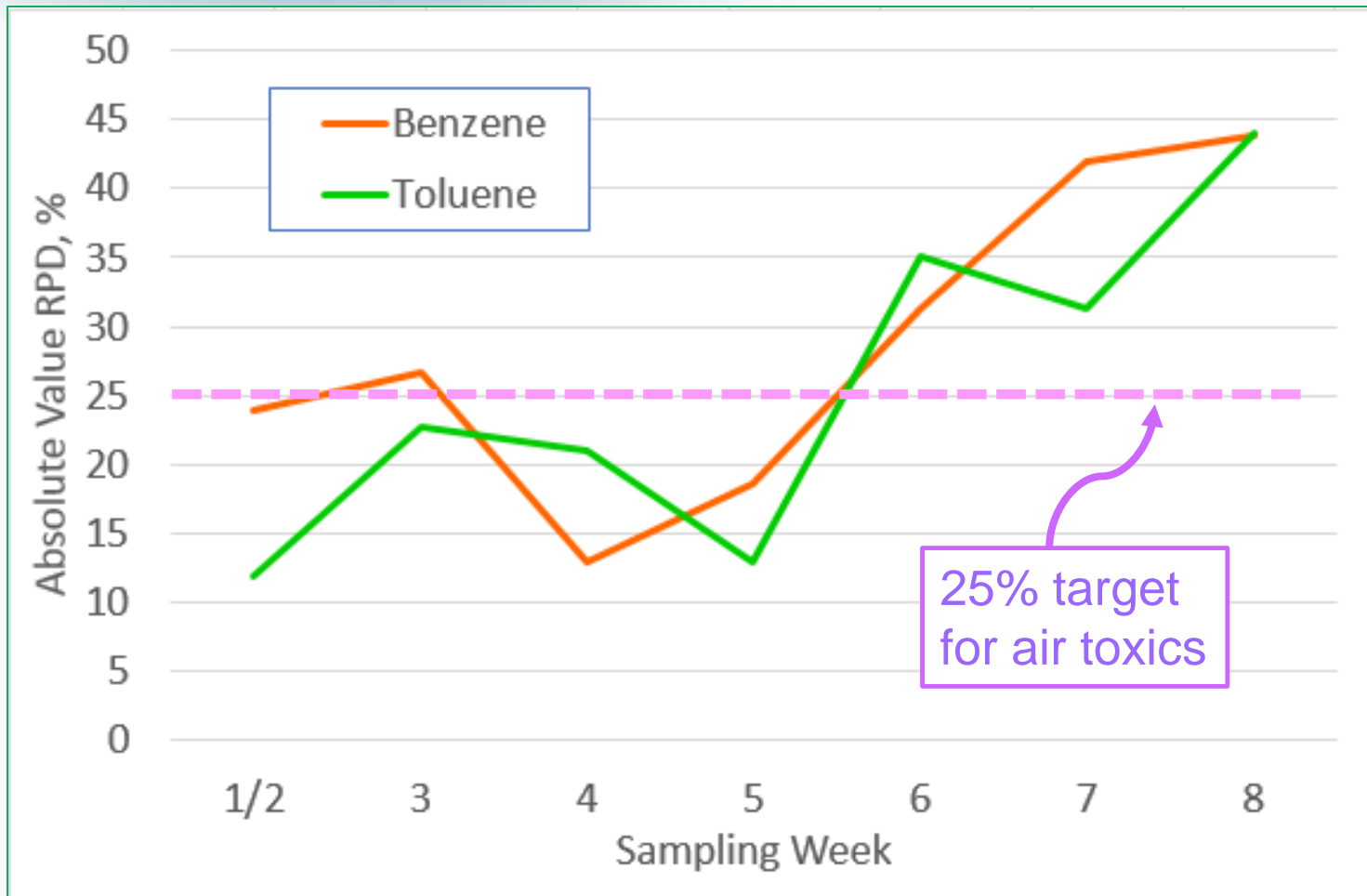


Toluene – Canister vs. Tube Regression

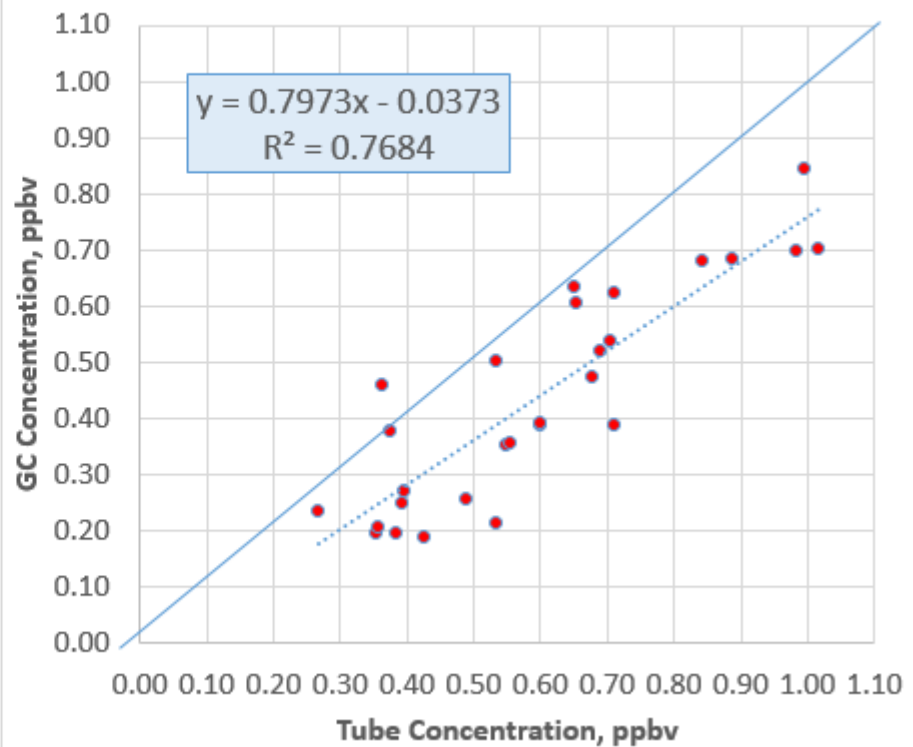
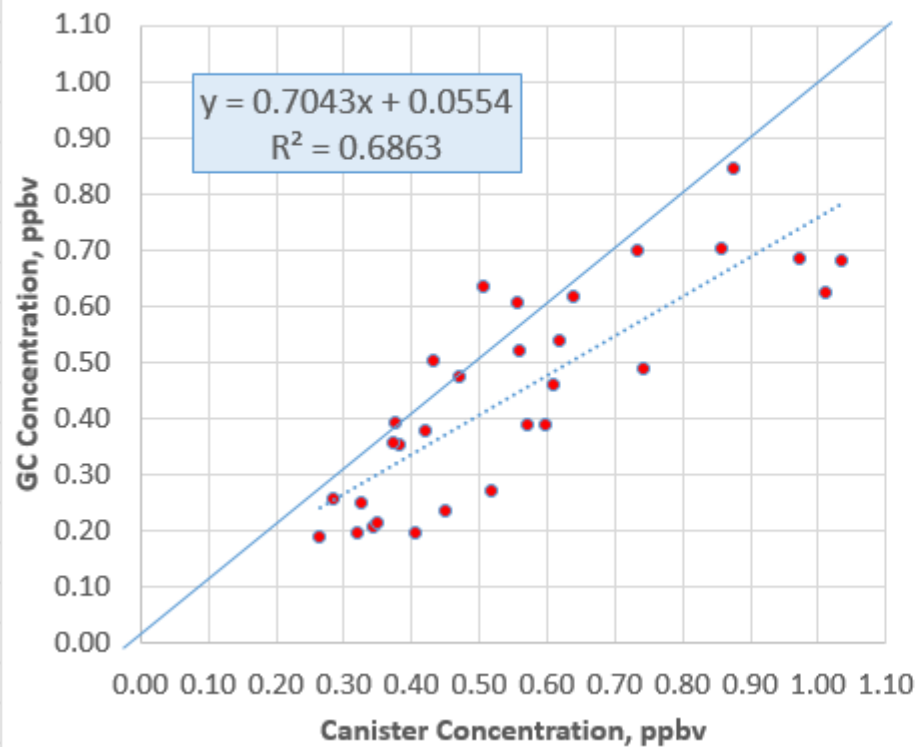


U.S. Environmental Protection Agency

Benzene and Toluene – Canister vs. Tube RPD



Toluene – Canisters & Tubes Compared with GC



Conclusions



- All three VOC monitoring methods compared within reasonable limits for both benzene and toluene.
- In general, the passive tube method resulted the highest concentrations and auto-GC the lowest.
- More field testing is recommended to confirm that these relationships hold up during extreme summer and winter weather conditions.

Acknowledgement



- We thank BP and their contractors for allowing us site access and the training/precautions needed to keep us safe while working at a very busy industrial site. The staff time allotted to escort us on-site is much appreciated.
- This project was made possible by in-kind laboratory services provided by EPA-CRL and EPA-ORD staff.